a ΔH of -3.0 was found. However, although this enthalpy change is more negative than that of reaction 5a, it seems clear that stabilization of NCD alone is not sufficient to account for the 9.0-kcal/mol difference in energy of isomerization between the parent NCD-CHT system and its dicyano counterpart. Indeed, destabilization of CHT appears to be even more important.

Conclusion

The ab initio calculations reproduce the experimental heats of isomerizations, where known, quite well. In addition, the model calculations on cyano-containing compounds provide a new interpretation of the effect of cyano substitution upon the NCD-CHT equilibrium.

We emphasize that all the ΔH values computed here are for the gas phase at 0 K. While the corrections to 298 K may be small, the solvent effects are influenced strongly by the difference in dipole moments of the two isomers, which is greatest in the case of benzene oxide-oxepin.

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Registry No. Ia, 544-25-2; Ib, 13612-59-4; Ic, 92720-75-7; Id, 291-70-3; Ie, 291-62-3; IIa, 14515-09-4; IIb, 92720-76-8; IIc, 1618-16-2; IId, 1488-25-1; IIe, 79010-90-5; $CH_2{=}CHCH_3$, 115-07-1; CH_3CH_3, 74-84-0; $CH_3C(CN)_2CH_3$, 7321-55-3; methylcyclopropane, 594-11-6; cyclopropane, 75-19-4.

Valence-Shell Electron-Pair Repulsions: A Quantum Test of a Naive Mechanical Model

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Abstract: The repelling points-on-a-sphere representation of the valence-shell electron-pair repulsion (VSEPR) theory implies the form of the potential energy surface for bending deformations in molecules. The degree to which such a surface actually resembles the Born-Oppenheimer surface of molecular orbital theory was examined for tetrahedral and octahedral binary compounds by using extended-Hückel and, in some cases, ab initio computations. With few exceptions among the molecules studied, the results of the simple mechanical model simulated the quantum results in quadratic, cubic, and higher order force constants to a remarkable degree when pairwise additive potential functions were assumed to fall off as r_{ij}^{-n}. Parameter n characterizing the hardness of repulsions was approximately 4 for ab initio surfaces; EHT, imposing frozen VOIP, gave harder forces with $n \simeq 6$. The present results show that the VSEPR model somehow captures the essence of molecular behavior to a degree heretofore not fully recognized.

Stereochemistry and molecular structure are accounted for quite successfully by a simple set of rules enunciated in the valence-shell electron-pair repulsion (VSEPR) theory.[1-3] According to this model the electron pairs (bond pairs and lone pairs) in the valence shell of a given main-group atom tend to be distributed in space in a way that imparts optimum mutual avoidance. A graphic representation often invoked is the likening of valence electron pairs to points-on-a-sphere (POS) that repel each other as if by some simple force law.[3-6] Such a model invites the following question. If the POS model is a bona fide model for structure, working for nonspurious reasons, why should it not afford a realistic representation of the potential energy surface for bending displacements of molecules as well?

No very thorough investigation of this possibility has yet been conducted. Perhaps the main reason for this neglect is that the model is usually thought of as being so oversimplified, better suited for freshman chemistry courses than for research, that it would be absurd to attribute more to it than utility as a teaching device. Another reason is that surprisingly little about the systematics of potential energy surfaces for bending is known. With rare exceptions, only quadratic constants for bending are available, and these are usually flawed by uncompensated effects of anharmonicity. Furthermore, in the most accurately studied cases, namely simple binary compounds AX_n, there are usually too few quadratic constants per molecule to provide the basis for a meaningful diagnosis in POS terms. For example, in AX_2 ($D_{\infty h}$), AX_4 (T_d), and AX_6 (O_h) molecules, there are only one, two, and three bending constants, respectively. Molecules with lower symmetry such as AX_5 (D_{3h}) with five constants, and AX_7 (D_{5h}), with seven, offer more interesting possibilities. Indeed, it was discovered, some time ago, once misassignments in the vibrational spectra had been corrected, that PF_5[4] and IF_7[6] do, in fact, exhibit characteristic POS aspects in the profiles of their quadratic bending constants. Furthermore, it was confirmed that the force law required to fit the IF_7 structure[7] (a pentagonal bipyramid with coupled e_2'' and e_1' deformations) is the same as the force law required to fit the profile of quadratic constants.[6]

A much richer source of information that would allow a more definitive test of the POS force field lies in the pattern of the contours of potential surfaces. A standard representation of the pattern is the set of Taylor series expansion coefficients for displacements, including higher order (anharmonic) as well as quadratic force constants. Simple molecules have many more anharmonic constants than harmonic. Unfortunately, too little

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Table I. Points-on-a-Sphere Force Constants $\tilde{f}^a$ for AX_6 Molecules

indices	$n = 5$	$n = 7$	indices	$n = 5$	$n = 7$	indices	$n = 5$	$n = 7$
44	1.014	0.858	456	−0.829	−0.933	444′4′	0.212	0.273
55	0.773	0.696	555	-5×10^{-4}	-9×10^{-4}	5555	0.167	0.230
66	0.572	0.548	566	−0.912	−0.986	555′5′	−0.353	−0.477
445	0.505	0.660	4444	0.105	0.135	6666	0.114	0.141

[a] Units of $2K/R^n$.

Table II. Geometric Mean[a] f_{ref} of Quadratic Force Constants for Bending, *aJ*

		f_{ref}			f_{ref}			f_{ref}
CF_4	STO-4G	1.509	SiF_4	EHT(d)[b]	0.637	CH_4	HF + cor[c]	0.574
CF_4	3-21G	1.671	SiF_4	EHT[d]	0.578	CH_4	HF[c]	0.627
CF_4	EHT	1.747	SiF_4	exp[e]	0.82	CH_4	EHT	0.743
CF_4	exp[e]	1.47	SF_6	EHT(d)[b]	2.356	CH_4	exp[f]	0.566
CCl_4	EHT[d]	2.148	SF_6	EHT[d]	2.434			
CCl_4	exp[e]	1.27	SF_6	exp[g]	1.993			

[a] Unweighted by degeneracy. [b] Calculation includes d orbitals on central atom. [c] Reference 22. [d] Calculation excludes d orbitals. [e] Reference 23. [f] Reference 11. [g] Heenan, R. K. Ph.D. Thesis, University of Reading, England, 1979.

has been known about bending anharmonicity to shed light on the VSEPR character of force fields. Not long ago, this situation changed.

Recent electron diffraction studies of very hot molecules of CF_4, SiF_4 and SF_6 could only be understood if it were assumed that bending deformations of large amplitude are decidedly anharmonic. In order to test the plausibility of this idea, cubic constants for bending modes were estimated from the quadratic constants via the POS model, for want of any better source of information. When this approach successfully explained the electron diffraction intensities,[9] it was decided to subject the POS model to further examination. For initial comparisons of the elementary POS mechanical model with a quantum mechanical model it seemed reasonable to apply extended-Hückel theory[10] (EHT), which had already been shown[5] to give quite realistic potential surfaces for bending. Tests of EHT, in turn, could be carried out in specific cases via ab initio molecular orbital calculations. An exploration of the merits of the POS model based on this approach is described in the following sections.

Procedure

Representation of Force Field. Potential energy surfaces will be expressed in this work as a function of the curvilinear symmetry coordinates $\tilde{S}_i$ for bending, conventions for which follow Robiette[11] for AX_4 and Vernon[12] for AX_6. Tabulated quadratic and cubic force constants are based on the Taylor expansions of the deformation energy

$$V - V_e = 1/2\sum_i\sum_j f_{ij}\tilde{S}_i\tilde{S}_j + V_{anh} \tag{1}$$

where, for AX_4 molecules

$$V_{anh} = 1/6\tilde{f}_{222}(\tilde{S}_{2a}{}^3 - 3\tilde{S}_{2a}\tilde{S}_{2a}\tilde{s}_{2b}{}^2) + 1/2\tilde{f}_{244}\{\tilde{S}2_a[s_{4z}{}^2 - (\tilde{S}_{4x}{}^2 + \tilde{S}_{4y}{}^2)/2] + ... + \tilde{f}_{444}\tilde{S}_{4x}\tilde{S}_{4y}\tilde{S}_{4z} + ...\} \tag{2}$$

and for AX_6

$$V_{anh} = \tilde{f}_{445}(\tilde{S}_{4x}\tilde{S}_{4y}\tilde{S}_{5z} + ...) + \tilde{f}_{456}[(\tilde{S}_{4y}\tilde{S}_{6x} + \tilde{S}_{4x}\tilde{S}_{6y})\tilde{S}_{5z} + ...] + \tilde{f}_{555}\tilde{S}_{5x}\tilde{S}_{5y}\tilde{S}_{5z} + \tilde{f}_{566}(\tilde{S}_{5z}\tilde{S}_{6x}\tilde{S}_{6y} + ...) + ... \tag{3}$$

Higher order contributions for deformations along specific directions $\tilde{S}_i$ are conveniently expressed in terms of the ratios $(2/m!)(\partial^m V/\partial\tilde{S}_i{}^m)/(\partial^2 V/\partial\tilde{S}_i{}^2)$ of Taylor coefficients found by differentiating polynomials fitted to numerical values of $V(\tilde{S}_i)$.

Points-on-a-Sphere Model. Valence shell electron pair repulsions are represented in the POS model by pairwise additive potential energy terms $V_{kl}(r_{kl})$ where r_{kl} is the distance between points k and l which are considered to move on the surface of a sphere of radius R. It is assumed, as a bookkeeping measure rather than as a physical assumption denying the relevance of bent bonds, that the electron-pair "points" lie exactly on the straight A–X bond lines. For the present purposes the V_{kl} components are taken to be of the form $r_{kl}{}^{-n}$ so that

$$V = K\sum_k\sum_{<l} r_{kl}{}^{-n} \tag{4}$$

where n is a measure of the "hardness" of valence-shell repulsions. Inasmuch as radius R can be absorbed into constant K, V is a two-parameter function. Instead of attempting specific optimizations of K and n, we shall fix the hardness parameter n at a value of 4 or 6 and compare ratios of force constants $\tilde{f}/f_{ref}$, where f_{ref} is the geometric mean of the quadratic force constants. In this way, for preset values of n, the POS potential surface can be compared with experiment or quantum computation in terms of dimensionless quantities with no adjustable parameters.

Analytical expressions for all POS quadratic and cubic constants for AX_4 molecules have been derived.[13] They are, in units of $(3/8)^{n/2}KR^{-n}$

$$f_{22} = n(n + 2)/8$$

$$f_{44} = n(n + 6)/8$$

$$\tilde{f}_{222} = -(6^{1/2}/192)n(n + 2)(n + 7)$$

$$\tilde{f}_{244} = -(6^{1/2}/96)(n^3 + 9n^2 + 6n)$$

and

$$\tilde{f}_{444} = 3n/4$$

A large set of corresponding constants for AX_6 molecules including a number of quartic constants has been deduced, partly in analytical and partly in tabulated form, by Bernstein and Vernon.[14] Analytical expressions for many of the constants have been published by Vernon.[12] Because these tabulations contain errors in $\tilde{f}_{445}$ and $\tilde{f}_{555}$ and did not include $\tilde{f}_{456}$, we list updated values in Table I.

Molecular Orbital Calculations. Potential energy surfaces were calculated numerically and fitted by least squares to yield the force constants of eq 1–3 and certain higher derivatives. Computations via EHT were carried out with ICON,[15] version 8, using observed bond lengths[16–18] and program default values for all parameters except for the scale factor K in the arithmetic mean H_{ij} element. This constant was taken as 2.00 instead of 1.75 because prelim-

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Table III. Reduced Force Constants $f^R \equiv \bar{f}/f_{\mathrm{ref}}$ for Bending Deformations in Tetrahedral Molecules: Comparisons of POS Model with Molecular Orbital Calculations[a] and Experiment

		$f_{22}{}^R$	$f_{44}{}^R$	$f_{222}{}^R$	$f_{244}{}^R$	$f_{444}{}^R$
POS	$n = 6$	0.816	1.225	−1.083	−2.000	0.612
CF_4	EHT	0.889	1.125	−0.957	−1.960	0.623
CCl_4	EHT	0.887	1.127	−0.956	−1.970	0.603
SiF_4	EHT(d)	0.837	1.195	−1.009	−1.911	0.810
SiF_4	EHT	0.873	1.145	−1.146	−2.162	0.619
CH_4	EHT	0.971	1.031	0.068	−0.760	0.794
POS	$n = 4$	0.775	1.291	−0.870	−1.528	0.775
CF_4	STO-4G	0.820	1.219	−0.748	−1.387	1.120
CF_4	3-21G	0.833	1.200	−0.710	−1.328	0.934
CF_4	exp[b]	0.82	1.21			
CCl_4	exp[b]	0.79	1.26			
SiF_4	exp[b]	0.77	1.30			
CH_4	exp[c]	1.032	0.969	0.166	−0.550	0.610
CH_4	HF[d]	1.024	0.976	0.156	−0.616	0.680
CH_4	HF, cor[d]	1.026	0.977			
POS	$n = 1$	0.655	1.528	−0.535	−0.713	0.750

[a] This research if source not identified. EHT excludes d orbitals unless (d) is listed. [b] Reference 23. [c] Reference 11. [d] Reference 22.

Table IV. Reduced Force Constants $f^R \equiv \bar{f}/f_{\mathrm{ref}}$ for Bending Deformations in SF_6: Comparisons of POS Model with Molecular Orbital Calculations and Experiment

	POS		EHT		
	$n = 1$	$n = 6$	including d	excluding d	expt[a]
$f_{44}{}^R$	1.853	1.279	1.145	1.099	1.289 (8)
$f_{55}{}^R$	0.974	1.011	1.014	0.973	0.940 (2)
$f_{66}{}^R$	0.554	0.774	0.861	0.935	0.825 (2)
$f_{445}{}^R$	0.419	0.784	0.756	0.871	1.01 (14)
$f_{456}{}^R$	−0.312	−1.187	−1.339	−1.396	
$f_{555}{}^R$	0.000	0.000	−0.122	−0.106	
$f_{566}{}^R$	−0.84	−1.279	−1.285	−1.355	
$f_{4444}{}^R$	0.047	0.165	0.165	0.143	
$f_{444'4'}{}^R$	0.080	0.326	n.c.[b]	0.401	
$f_{5555}{}^R$	0.048	0.274	0.268	0.318	
$f_{555'5'}{}^R$	−0.119	−0.571	−0.530	n.c.[b]	
$f_{6666}{}^R$	0.074	0.175	0.160	0.177	

[a] Heenan, R. K. Ph.D. Thesis, University of Reading, England, 1979. [b] Not calculated.

inary calculations suggested that the higher value gave somewhat better bending force constants. Although later calcultations showed that $K = 2.00$ is by no means optimum for all molecules, the calculations also showed that the dimensionless ratios sought are insensitive to K. This insensitivity is consistent with prior experience.[19] For CF_4 ab initio computations at the STO-4G[20] and 3-21G[21] levels were performed. Ab initio[22] and experimental[11] values of quadratic and cubic constants for CH_4 are in the literature.

Because the dimensionless quantities, tabulated in the next section to allow simple and direct comparisons of the various force fields, do not convey the absolute values of the force constants derived, we list the mean quadratic constants (i.e., f_{ref}), computed and experimental,[11,23] in Table II. From these and the tabulated ratios can be reconstructed absolute values of all constants.

Results

Quadratic and cubic force constants $f^R \equiv \bar{f}/f_{\mathrm{ref}}$ corresponding to the POS model are compared with MO and, where available, experimental constants for a series of tetrahedral molecules in Table III. Similar comparisons including several quartic constants, as well, are offered in Table IV for the octahedral molecule

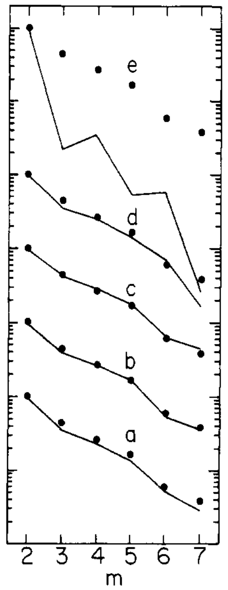

Figure 1. Higher order potential constants $|(\partial^m V/\bar{S}_{2a}{}^m)/m!|$ divided by the quadratic constant $(\partial^2 V/\partial\bar{S}_{2a}{}^2)/2$, for e symmetry coordinate $\bar{S}_{2a}$, logarithmic scale. Dots, POS field; lines, EHT. Molecular orbital calculations: a, CF_4; b, SiF_4 (including d on Si); c, SiF_4 (excluding d); d, CCl_4; e, CH_4. For odd m both POS and EHT constants were negative.

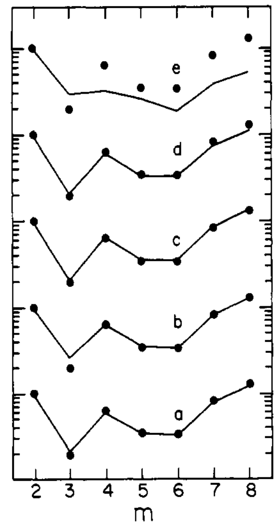

Figure 2. Higher order potential constants $(\partial^m V/\partial\bar{S}_{t_2}{}^m)/m!$ divided by the quadratic constant, for t_2 symmetry coordinate $\bar{S}_{t_2} = (\bar{S}_{4x} + \bar{S}_{4y} + \bar{S}_{4z})/3^{1/2}$, logarithmic scale. Points, POS; lines, EHT; for labels, see caption of Figure 1.

SF_6. More as a test of sensitivity to parameterization than as a diagnosis of physical significance, EHT computations involving sulfur and silicon were carried out with and without valence-shell d-orbitals. Because quartic and higher order potential constants rapidly proliferate the higher the order, only a few selected aspects of these heretofore little-studied features of the potential surfaces were examined. Plotted in Figures 1 and 2 for tetrahedral molecules as a function of m are the Taylor series coefficients $(\partial^m V/\partial S_i{}^m)/m!$ along specific directions in the space of the e and t_2 symmetry coordinates. For these comparisons with POS only EHT values are available. Somewhat analogous tables and plots of quadratic constants for PF_5 and IF_7 can be found.[4,7,24]

Of all the examples yet studied, methane is in conspicuously poorest agreement with the POS model. The reason for this is not altogether clear. The closest alkane, ethane, has been found in quadratic and cubic constants to conform far more closely to

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a model of geminal repulsions.[25]

Discussion

On balance, the successes of the POS model in simulating molecular orbital computations of potential energy surfaces for bending are far more noteworthy than the failures. Even the difference in hardness of repulsion required to represent the semiempirical EHT fields ($V_{ij} \sim r_{ij}^{-6}$) and ab initio fields ($V_{ij} \sim r_{ij}^{-4}$) is plausible. That EHT yielded the more steeply changing energies is consistent with the fact that its parameterization was frozen instead of being allowed to relax to compensate for shifts in charge accompanying bending deformations. Also satisfying is the fact that the repulsion law accounting for the present AX_4 and AX_6 force fields is the same as that previously needed[4,6] for force fields of AX_5 and AX_7 and, as well, the detailed structure of the latter case[7] (structures of AX_4, AX_5, and AX_6 being independent of the POS law).

While it is gratifying that the POS results agree as well as they do with the molecular orbital calculations, it must be admitted that the present molecular orbital calculations were carried out at a comparatively low level. This was entirely consistent with the exploratory nature of the research. Expensive computations of so many potential constants was hardly warranted before it was learned whether the POS model is worth such an investment. As can be seen in Table II, absolute values of the force constants, which for the EHT depend heavily on K, vary appreciably. Nevertheless, it is important to note that in the dimensionless quantities characterizing the contours of the potential surfaces (Tables III and IV), corresponding molecular orbital and experimental constants are in reasonable agreement with each other.

Clearly, the valence-shell electron-pair repulsion theory in its elementary repelling points-on-a-sphere formulation mimics quantum computations too successfully to be dismissed as spurious. It is apparent that occupied bond orbitals are guided by quantum laws to avoid each other in space. This reluctance to overlap corresponds to a force law that is substantially harder than Coulombic but softer than that corresponding to nonbonded atom–atom repulsions. Moreover, even though atom–atom repulsions would formally give rise to a POS-like field (in the absence of lone pairs), computations of the magnitudes of such repulsions have indicated that they are too small to account for observed harmonic and anharmonic constants.[6,26,27] Empirical evidence, then, tends to corroborate the original rationale of Gillespie and Nyholm[2] who attributed the avoidance to the action of Pauli's principle in the valence shell of the central atom. While this is probably correct as far as it goes, it does not draw attention to the manifestly covalent aspect of the energetics. As pointed out elsewhere,[28] optimization of the aggregate covalent overlap goes hand in hand with the mutual avoidance of the electron-pair bonds. A more definitive theoretical treatment of the underlying principles would be desirable. The case of methane, the simplest of the molecules so far treated yet the most out of step with POS model, serves as a warning against glib generalizations.

Whatever the ultimate explanation and range of applicability of the POS model, it is evident that the model manages to reproduce quite well a large body of information. For this reason it shows promise in a variety of applications. It seems to offer a simple yet more reliable scheme than those frequently adopted by spectroscopists in assigning vibrational frequencies. It can provide quick estimates of anharmonic potential constants for bending if the harmonic constants are known. It yields reasonable treatments of certain dynamic properties of molecules such as Berry pseudororotation in trigonal bipyramids and Pitzer pseudorotation in pentagonal bipyramids.[4,6,26] It was able to account for anomalies in the diffraction patterns of very hot molecules.[8,9] Certainly the valence shell electron pair repulsion theory in its repelling Points-on-a-Sphere representation is much more than a pedagogical aid. It deserves thoughtful consideration by experimentalists and theorists, alike.

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Intramolecular Proton Exchange in Near Symmetric Cases

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Abstract: We present a simple theoretical model for describing tunnelling of a particle in a symmetric and in an asymmetric double-minimum potential. In the case of an asymmetric double-minimum potential the tunnelling is described by a parameter ρ, which is the ratio between the difference in energy between the particle energies in the two wells and the difference in energy between the lowest two eigenstates E_g and E_u of the corresponding symmetric case. In the asymmetric case, only the fraction $(1 + \rho^2)^{-1}$ of the particle tunnels. The frequency of exchange is increased by a factor $(1 + \rho^2)^{1/2}$ with respect to the corresponding symmetric case.

We have confirmed in a series of calculations[1-3] the well-known result that a particle in a symmetric double-minimum potential will tunnel back and forth between the two wells A and B (Figure 1a). Our calculations give the rate of exchange in intramolecular hydrogen-bonded species such as malonadlehyde[4] and naphthazarin.[5] We also presented evidence that tunnelling is drastically reduced or eliminated when a slight asymmetry is introduced.[2] This evidence was used to explain the strong coupling of the rotation of the methyl group with the rate of proton exchange in

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